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Coloured glass substrate carrying a coating

The present invention relates to a glazing comprising:

- a substrate made of coloured soda-lime glass composed of main glass-forming constituents and of colouring agents,
- a coating deposited on the coloured glass substrate.

The expression "soda-lime glass" is used here in the broad sense and relates to any glass which comprises the following constituents (percentages by weight):

SiO ₂	60 to 75%
Na ₂ O	10 to 20%
CaO	0 to 16%
K ₂ O	0 to 10%
MgO	0 to 10%
Al ₂ O ₃	0 to 5%
BaO	0 to 2%
BaO + CaO + MgO	10 to 20%
K ₂ O + Na ₂ O	10 to 20%.

This type of glass finds very wide use in the field of glazings for motor vehicles or buildings, for example. It is commonly manufactured in the form of a ribbon by the float-glass process. Such a ribbon can be cut in the form of sheets, which can subsequently be bent or subjected to a treatment for enhancing the mechanical properties, for example a thermal tempering treatment.

When referring to the optical properties of a glass sheet, it is generally necessary to relate these properties to a standard illuminant. In the present description, two standard illuminants are used: Illuminant C and Illuminant A defined by the Commission Internationale de l'Eclairage (C.I.E.) [International Commission on Illumination]. Illuminant C represents average daylight having a colour temperature of 6700 K. This illuminant is especially of use in evaluating the optical properties of glazings intended for buildings. Illuminant A represents the radiation from a Planck radiator at a temperature of approximately 2856 K. This illuminant represents the light emitted by car headlamps and is especially intended to evaluate the optical properties of glazings intended for motor vehicles.

The "light transmission factor" (LT) is the percentage of incident luminous flux transmitted in the visible region, between 380 and 780 nm, through a substrate.

The "light reflection factor" (LR) is the percentage of incident luminous flux reflected by a substrate.

The "ultraviolet transmission factor" (UVT4) is the total percentage of transmission in the ultraviolet, between 290 nm and 380 nm, for a glass with a thickness of 4 mm.

The "energy transmission factor" (ET) is the total percentage of incident energy radiation directly transmitted through a substrate between the wavelengths 300 and 2500 nm.

The "solar factor" (SF) is the sum of the total energy directly transmitted through a substrate (ET) and of the energy which is absorbed (AE) and reradiated at the face opposite the energy source, with respect to the total energy radiation reaching the substrate.

The "selectivity" of a coated substrate represents the ratio between the light transmission factor and the energy transmission factor. It can be defined as being the ratio of the light transmission factor to the solar factor (LT/SF), which is used in particular in the case of a building glazing. It can also be defined as being the ratio of the light transmission factor to the energy transmission factor (LT/ET), in particular in the case of glazings for vehicles, for which the energy which is absorbed and reradiated is regarded as negligible when the vehicle is in motion.

The "dominant wavelength" (λ_D) is the peak wavelength in the range transmitted or reflected by the coated substrate.

The "purity" (P) of the colour of the substrate refers to the excitation purity measured using Illuminant C. It is defined according to a linear scale in which a defined source of white light has a purity of 0 and the pure colour has a purity of 100%. The purity of a coated substrate is measured on the side opposite the coated face.

The "emissivity" (ϵ) is the ratio of the energy emitted by a given surface at a given temperature to that of a perfect radiator (black body having an emissivity of 1.0) at the same temperature.

From a technical viewpoint, it is desirable for the glazing, when subjected to sunshine, not to allow too great a proportion of the total incident solar radiation to pass through, in order for the interior of the vehicle or building not to become overheated.

One of the objectives of the present invention is to obtain a glazing which exhibits a high level of solar protection combined with a high selectivity and which can be obtained under conventional industrial manufacturing conditions.

It has been discovered that this objective, and others, can be achieved by a glazing which combines a selective coloured glass substrate, which

exhibits a selectivity (LT/ET) of at least 1.1, measured with Illuminant C for a glass thickness of 4 mm, and a pyrolytic coating which provides the coated glazing with an increased selectivity with respect to the selectivity of the uncoated coloured glass. In the context of the present invention, the glazing comprises a coloured glass substrate.

The present invention makes it possible to obtain a glazing exhibiting a high selectivity while avoiding the difficulties which are often associated with the industrial manufacture of coloured glasses of high selectivity. In addition, the present invention makes possible a greater flexibility in manufacturing in the sense that it is generally easier to modify the properties of the glazing by changing the coating rather than by modifying a coloured glass composition.

The coloured glass is preferably chosen so that its selectivity has a value of at least 1.3. This contributes to easily obtaining a coated glazing of high selectivity.

However, the selectivity of the uncoated coloured glass is preferably less than or equal to 2. It is possible for uncoated coloured glasses to have a selectivity of greater than 2; however, these are generally difficult to obtain under conventional industrial manufacturing conditions for two reasons: a high content of iron needed in order to obtain the high selectivity renders the glass difficult to melt, which then requires the use of particular electric furnaces, which are of low-capacity and, furthermore, a high redox ratio of FeO/total Fe which is favourable to the achievement of a high selectivity requires modifying the refining conditions, which renders the preparation of the glass problematic under industrial manufacturing conditions. This is why the selectivity of the uncoated coloured glass is preferably less than or equal to 2.

The coloured glass is preferably a glass for which the transmission between the wavelengths 1000 and 1200 nm, for a thickness of 4 mm, is lower by at least 5 points (expressed as %: ratio of the transmitted radiation to the incident radiation) with respect to the transmission between the wavelengths 500 and 600 nm. A coloured glass which meets this condition is selective and can in particular be green, blue or grey.

The coloured glass can be a soda-lime glass coloured dark grey composed of main glass-forming constituents and of colouring agents, in which glass the elements iron, selenium, cobalt and chromium are present as colouring agents in an amount corresponding to the following proportions (expressed as percentage by weight of the glass as if they are present in the form shown)

Fe ₂ O ₃	0.75 to 1.8%
Co	0.0040 to 0.0180%

Se	0.0003 to 0.0040%
Cr ₂ O ₃	0.0010 to 0.0100%

and the proportions of the colouring agents are such that the glass exhibits a total energy transmission, measured for a thickness of 4 mm (ET4), of
 5 between 15 and 40%, a selectivity (LTA/ET4) of at least 1.2 and an excitation purity (P) not exceeding 10%.

As an alternative form, the coloured glass is a green-coloured soda-lime glass which comprises the following percentages by weight of colouring agents, the total amount of iron being expressed in the form of Fe₂O₃:

10	Fe ₂ O ₃	0.7 to 1.3%
	FeO	0.18 to 0.27%
	Co	0 to 0.0040%
	V ₂ O ₅	0.0050 to 0.1%, and which exhibits,
15	under Illuminant A and for a glass thickness of 4 mm, a light transmission (LTA4) of between 40 and 70% and a selectivity (LTA/ET4) of greater than or equal to 1.50.	

According to another preferred embodiment of the invention, the coloured glass is a grey-green soda-lime glass composed of main glass-forming constituents and of colouring agents which comprises less than 0.4% by weight of FeO and from 0.9 to 1.8% of Fe₂O₃, which has an excitation purity of more than
 20 5% and which exhibits, under Illuminant A and for a glass thickness of 4 mm, a light transmission (LTA4) of greater than 30%, a selectivity (LTA/ET) of greater than 1.55 and an ultraviolet radiation transmission (UVT4) of less than 10%.

As an alternative form, the coloured glass is a coloured soda-lime glass composed of main glass-forming constituents and of colouring agents which
 25 comprises from 0.40 to 0.52% by weight of FeO and which exhibits, under Illuminant A and for a glass thickness of 4 mm, a light transmission (LTA4) of less than 70%, a selectivity (LTA/ET4) of greater than 1.65 and an ultraviolet radiation transmission (UVT4) of less than 8%.

A particularly pleasing aesthetic appearance in combination with a
 30 high selectivity can also be obtained with a coloured soda-lime glass with a blue hue composed of main glass-forming constituents, including more than 2% of magnesium oxide, and of colouring agents which comprises more than 1.1% by weight of Fe₂O₃, less than 0.53% by weight of FeO and less than 0.13% of manganese oxide, which has a light transmission (LTA4) of between 15% and 70%
 35 and a selectivity (SE4) of greater than 1.2, and which exhibits a dominant wavelength (λ_D) and a purity (P) such that they lie in a CIE trichromatic diagram inside a triangle, the tips of which are defined by the points representing Illuminant C and the points with the (λ_D , P) coordinates (490,19) and (476,49) respectively.

In order to obtain a higher value of selectivity and/or a significant improvement in the selectivity with respect to the starting uncoated coloured glass, the selectivity is preferably increased by at least 3% with respect to the selectivity of the uncoated coloured glass. The selectivity is preferably increased by at least 10% with respect to the selectivity of the uncoated coloured glass.

Various techniques are known for forming coatings on a substrate made of vitreous material, including pyrolysis and cathodic sputtering. The coating of the present invention is a coating deposited by pyrolysis. Pyrolysis generally exhibits the advantage of forming a hard coating which does not require a protective layer. Coatings formed by pyrolysis exhibit lasting properties of resistance to abrasion and corrosion. It is believed that this is due in particular to the fact that the process comprises the deposition of precursor on a substrate which is hot. Furthermore, pyrolysis is generally less expensive than other coating processes, such as cathodic sputtering, particularly in terms of investment in equipment. This is because deposition by pyrolysis can be carried out continuously during the manufacture of the glass on the freshly formed hot glass ribbon. In contrast, a deposition such as by cathodic sputtering is carried out under vacuum away from the manufacturing line on cold glass cut up beforehand into sheets. In addition, the deposition of coating by processes other than pyrolysis, for example by cathodic sputtering, results in products which exhibit different properties, in particular a decreased resistance to abrasion and sometimes different optical properties (refractive index).

The coating deposited by pyrolysis can be applied to the substrate by chemical vapour deposition or starting from a liquid precursor. The coating (or the coating layers) is preferably applied to the substrate by chemical vapour deposition. Chemical vapour deposition is particularly preferred because it tends to produce coatings with an even thickness and composition, the uniformity of the product being particularly important when the glazings have to be used for large surface areas. With the use of liquid reactive materials, it is not possible to influence the evaporation process, which renders it random. In addition, chemical vapour deposition is more economic from the viewpoint of the utilization of the starting materials, which results in decreased wastage.

The coating is preferably such that its transmission between the wavelengths 500 and 600 nm on clear glass with a thickness of 4 mm is higher by at least 3 points (expressed as percentage: ratio of the transmitted radiation to the incident radiation) with respect to the transmission between the wavelengths 1000 and 1200 nm.

Such a coating also makes it possible to obtain a selective glazing with clear glass.

Preferably, the coating is chosen from the following:

- coating deposited by pyrolysis comprising tin and antimony in a molar ratio Sb/Sn of between 0.01 and 0.5,
- oxide coating deposited by pyrolysis comprising a conductive or semiconductive layer with a thickness of 15 to 500 nm formed from a material comprising a metal oxide comprising a doping agent in a ratio of 5 to 100 mol per 100 mol of metal oxide, the metal oxide being selected from one or more of the following: tungsten oxide (WO_3), molybdenum trioxide (MoO_3), niobium pentoxide (Nb_2O_5), tantalum pentoxide (Ta_2O_5), vanadium pentoxide (V_2O_5) and vanadium dioxide (VO_2),
- coating deposited by pyrolysis which comprises an anti-reflective interferential stacking which comprises, from the glass, a stacking of materials with alternatively high and low refractive indices,
- coating deposited by pyrolysis which comprises a layer with an emissivity of less than 0.3, in particular a layer deposited by pyrolysis based on fluorine-doped tin oxide
- titanium nitride coating deposited by pyrolysis. It can be in the form of a stacking based on titanium nitride layer, which may be oxidised.

It has been discovered that such coatings are particularly suitable for increasing the selectivity of the glazing with respect to the selectivity of the uncoated coloured glass.

Oxide coatings deposited by pyrolysis comprising tin and antimony in a molar ratio Sb/Sn of between 0.01 and 0.5 are disclosed in particular in Patent Applications GB 2,302,102 and GB 2,302,101, the contents of which are incorporated in the present application by way of reference. Such coatings provide an increase in selectivity ranging up to 20%.

Coatings deposited by pyrolysis can comprise a conductive or semiconductive layer with a thickness of 15 to 500 nm formed from a material comprising a metal oxide comprising a doping agent in a ratio of 5 to 100 mol per 100 mol of metal oxide, the metal oxide being selected from one or more of the following: tungsten oxide (WO_3), molybdenum trioxide (MoO_3), niobium pentoxide (Nb_2O_5), tantalum pentoxide (Ta_2O_5), vanadium pentoxide (V_2O_5) and vanadium dioxide (VO_2). Such coatings provide an increase in selectivity ranging up to 30%. In addition, they make possible a considerable increase in the selectivity in terms of LT/SF ratio: the selectivity of the glazing can be more than 30% greater than the selectivity of the uncoated coloured glass.

The coating can comprise a layer with an emissivity of less than 0.3. A layer of oxide comprising tin and antimony in a molar ratio Sb/Sn of between 0.01 and 0.5 described above can possess this property. As an alternative form, the layer of low emissivity can be a layer based on fluorine-doped tin oxide. A layer with a low emissivity makes it possible to increase the selectivity in terms of LT/SF ratio, as the emissivity affects the value of the solar factor: a low emissivity makes it possible to decrease the solar factor of the glazing and thus to increase the selectivity calculated in terms of LT/SF ratio.

The coating can comprise an underlayer between the substrate and the coating deposited by pyrolysis. This underlayer can also be deposited by pyrolysis. The role of such an underlayer can be to reduce the haze by preventing the migration of sodium ions from the glass, by diffusion or by any other way, to the coating layer, whether during the formation of this upper layer or during a subsequent high-temperature treatment. For example, such an underlayer can be formed of a silicon oxide having a geometric thickness of approximately 100 nm. Such an underlayer is not generally necessary for glazings with a low light transmission factor as in such cases the haze is not apparent to a significant extent. Another role of an underlayer, as an alternative form or in addition to the role set out above, can be to form an "anti-reflecting" stacking, for example by means of an aluminium/vanadium oxidized underlayer, as disclosed in Patent Application GB 2,248,243.

In preferred embodiments of the invention, the coating is a coating deposited by pyrolysis, preferably deposited in the vapour phase, which comprises tin and antimony in a molar ratio Sb/Sn of between 0.04 and 0.16. It has been discovered that coatings comprising such proportions of tin and antimony make it possible to produce glazings, the high selectivity properties of which are particularly advantageous: the increase in selectivity of the coated glazing with respect to the uncoated coloured glass is generally at least 7% and often more than 10%.

The oxide coating deposited by pyrolysis, which comprises tin and antimony in a molar ratio Sb/Sn of between 0.01 and 0.5, preferably has a thickness of between 250 and 500 nm. Such thicknesses can be obtained under conventional industrial manufacturing conditions, whereas thin or very thick coatings are difficult to produce in practice, and these thicknesses make it possible to obtain increases in selectivity which can be very large, for example more than 20%, with respect to the coloured glass alone without coating.

For some applications, it is necessary for the coated substrate to be subjected to a subsequent treatment during which it is bent and/or heat treated, in particular annealed or tempered. This is particularly the case with motor vehicle

glazings. The glazing according to the invention preferably withstands this treatment, in particular if the coating is deposited by pyrolysis. In this case, its properties are not significantly modified by the subsequent treatment. As an alternative form, if it is a coating deposited by cathodic sputtering, it is sufficient for this coating to comprise one or more so-called "sacrificial" layers which make it possible to protect the active layer or layers during the subsequent treatment.

The light reflection factor (LR) of the glazing is generally low, which is particularly advantageous for vehicle glazings. The light reflection factor (LR) of the glazing is preferably less than 13%.

The emissivity of the glazing is preferably less than 0.2. The emissivity affects the value of the solar factor: a low emissivity makes it possible to decrease the solar factor of the glazing and thus to increase the selectivity calculated in terms of LT/SF ratio. On the other hand, a low emissivity coating is generally not as good as antisolar coatings to decrease the energy transmission factor thus to increase the selectivity calculated in terms of LT/ET.

The selectivity of the coated substrate can be very high and it is preferably greater than 2. A glazing with such high selectivity is particularly desired for reasons of comfort in the field of automobile glazings.

It has been discovered that the glazing according to the invention can exhibit a dominant transmitted wavelength in the visible spectrum of the coated substrate which is less than the dominant transmitted wavelength of the uncoated substrate, preferably by at least 1, 2, 3, 4, 5 nm or even more. This is particularly advantageous when the coloured glass has a transmitted colour which is not greatly appreciated aesthetically: a typical example is green glass, having a dominant transmitted wavelength which is between 490 and 550 nm and more particularly between 490 and 520 nm. Such a glass is obtained by addition of iron to the composition of the glass. The iron makes it possible to obtain very high selectivities but the increase in the amount of iron in the composition, in combination with an increase in the selectivity, also increases the green appearance in transmission, which is generally not greatly appreciated for aesthetic reasons. The present invention makes it possible to overcome this disadvantage by providing a glazing for which the dominant transmitted wavelength is less than the dominant transmitted wavelength of the coating-free coloured glass and therefore a glass which will have a less green and more bluish appearance than the starting coloured glass, which is regarded as more desirable from an aesthetic viewpoint. It has been discovered that this advantage is particularly achieved when the coating is a coating deposited by pyrolysis comprising tin and antimony in a molar ratio Sb/Sn of between 0.01 and 0.5 and more particularly a coating deposited by pyrolysis,

preferably deposited in the vapour phase, which comprises tin and antimony in a molar ratio Sb/Sn of between 0.04 and 0.16, preferably between 0.08 and 0.14. Such a glazing additionally exhibits the advantage of having advantageous energy properties because such a coating reflects in particular wavelengths situated in the far infrared, whereas the coloured glass absorbs in particular in the near infrared: there is therefore a complementary effect which is highly favourable to the selectivity of the assembly.

Consequently and preferably, the dominant transmitted wavelength in the visible spectrum of the coated substrate is less than 500 nm, preferably less than or equal to 495 nm, preferably in combination with a purity of less than 20%.

The glazing according to the invention is particularly suitable as vehicle glazing. In particular, it can be used as motor vehicle or train glazing.

One particular application of the invention is in the possibility it provides in providing an advantageous combination of properties in a glazing for solar control applications. In this respect:

- The coating may be such that if applied to 4 mm thick clear glass the so coated glass would have a light transmission factor measured with illuminant C of less than or equal to 70%, 65%, 60%, 55%, 50%, 45%, 40% or 35%.
- The coating may be such that if applied to 6 mm thick clear glass the so coated glass would have a light transmission factor measured with illuminant C of less than or equal to 65%, 60%, 55%, 50%, 45%, 40% or 35%.
- The coating may reduce the light transmission factor of the coated glazing such that the ratio of the light transmission factor of the coated glazing divided by the uncoated glass substrate is less than 0.9, 0.85, 0.8, 0.75, 0.7, 0.65, 0.6, 0.55 or 0.5 in which the light transmission factor is preferably measured using illuminant C.
- The coating may reduce the light transmission factor of the coated glazing by greater than 10%, 12%, 14%, 15%, 16%, 17%, 18%, 19%, 20%, 21%, 22%, 23%, 24%, 25%, 26%, 27%, 28%, 29%, 30%, 31%, 32%, 33%, 34%, 35%, 36%, 37%, 38%, 39% or 40% with respect to the uncoated glass substrate calculated according to the formula

$$\frac{LT_{\text{uncoated substrate}} - LT_{\text{coated glazing}}}{LT_{\text{uncoated substrate}}} \times 100.$$

in which LT is preferably measured using illuminant C.

Such advantages may be achieved using a glass substrate having a thickness of, for example about 2mm, 4mm, 6mm, 8mm, 10mm, 12mm or more.

The invention will now be described in more detail with reference to the following nonlimiting examples.

The properties of the various types of coloured glass are presented in Table 1 below. The properties are measured on glass samples with a thickness of 4 mm. For some glasses, the properties for a thickness of 6 mm are mentioned, in addition. The initials in this table and in the other following tables (LTA, UVT4, LTC, ET, and the like) have the meanings described above. In addition, the main colouring agents present in the various coloured glasses are mentioned in Table 1.

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Year	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	

Table 1

Type of glass	Green	Dark green	Very dark green	Grey 1	Grey 2	Blue 1	Blue 2
Thickness	4 mm 6 mm	4 mm 6 mm	4 mm 6 mm	4 mm	4 mm	4 mm	4 mm
Wavelength	504 504	498 499	496 496	494	495	489	486
(III C) (nm) trans.							
Purity (III C)(%)	3.5 5.2	7.7 11	11.2 15.8	5.8	5	16.8	24.3
LTA (%)	65.3 55.3	45.3 32.2	32.2 19.4	35.4	48.1	42.7	36.94
UVT4		<10	2.9				
		%					
LTC (%)	67 57.42	47.5 34.5	34.3 21.3	36.5	49.4	45.3	39.9
ET CIE (%)	38.6 28.4	25.2 15.7	17.7 9.5	26.3	34.6	26	21.4
SF	52.8 45.2	42.9 35.8	37.3 31.3	43.7	49.9	43.5	40.1
LTC/ET	1.74 2.02	1.88 2.20	1.94 2.24	1.39	1.43	1.74	1.86
LTC/SF	1.27 1.27	1.11 0.96	0.92 0.68	0.84	0.99	1.04	1
Colorants:							
Fe ₂ O ₃ (%)	0.94	1.32	1.55	1.4	1.13	1.26	1.24
(FeO calc %)	0.24	<0.4	0.44				
Co (ppm)	7	43	80	94	61	67	81
V ₂ O ₅ (ppm)	153	238	429	imp.	imp.	7	imp.
Cr ₂ O ₃ (ppm)	imp.	133	214	17	23	77	imp.
Se (ppm)	imp.	imp.	imp.	8	imp.	imp.	imp.

imp. = impurities

EXAMPLES 1 to 5, Comparative Examples 1 and 2

"Green"-coloured float glass as defined in Table 1, progressing along a float tank, is coated by CVD (Chemical Vapour Deposition) pyrolysis by means of a reactant comprising a mixture of MBTC (monobutyltrichlorotin) as source of tin and of SbCl_3 as source of antimony. The reactant mixture is vaporized in a stream of anhydrous air at approximately 200°C . The vaporization is facilitated by the nebulization of these reactants in the carrier gas. Superheated steam at approximately 200°C is subsequently introduced.

The coating process is continued until the geometric thickness of the tin/antimony oxide coating overlying the substrate is approximately 280 nm (Examples 1 to 3) or 440 nm (Examples 4 and 5). The Sb/Sn molar ratio in the coating, measured by X-ray fluorescence, is mentioned in the table, as well as the thicknesses, also measured by X-ray fluorescence.

As Comparative Example 1, similar glass is coated with an absorbent layer with a thickness of approximately 45 nm, deposited by pyrolysis, formed of a mixture of Fe, Co and Cr oxides in the proportions by weight 26% Fe_2O_3 , 61% Co_3O_4 and 13% Cr_2O_3 .

As Comparative Example 2, similar glass is coated with a layer of approximately 55 nm, deposited by pyrolysis, comprising titanium and tin oxides (90% TiO_2 by weight and 10% SnO_2 by weight).

Table 2 shows that, for the comparative examples, the selectivity is decreased with respect to the selectivity of the starting glass, whereas the dominant transmitted wavelength and the purity are increased, which provides an even more marked green appearance regarded as unfavourable from an aesthetic viewpoint. In contrast, for Examples 1 to 5, the selectivity is markedly increased with respect to the selectivity of the coloured glass alone: an increase of up to 19%. Furthermore, the dominant transmitted wavelength is less than that of the coloured glass alone, which is favourable from the viewpoint of the desired properties.

The light reflection (LR) and solar factor (SF) values are measured on the coated/uncoated side.

The coating of example 1 in Table 2 reduces the light transmission factor of the coated glazing by 25.4% with respect to the uncoated glass substrate calculated according to the formula:

$$\frac{LT_{\text{uncoated substrate}} - LT_{\text{coated glazing}}}{LT_{\text{uncoated substrate}}} \times 100.$$

$LT_{\text{uncoated substrate}}$

This may be calculated as follows:

TLC of uncoated 4mm Green glass:

67% (from Table 1)

TLC of coated 4mm Green glass according to example 1:

50% (from Table 2)

Absolute reduction in TLC due to coating: $67\% - 50\% = 17$

Reduction in TLC due to coating with respect to the uncoated substrate:

$(17/67) \times 100 = 25.4\%$

5

As an alternative form, the results are given here for an identical coloured glass with a thickness of 6 mm instead of 4 mm, in Table 3.

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Table 2

Example	Green glass, 4 mm, LT/ET glass alone = 1.74							
	LTC	λ_D tr	P	ET	SF	LR	LT/ET	% difference
Comparative 1	28.4	567	13	18.8	33/36	34/17	1.51	-0.23
Comparative 2	50	550	5.8	29	41/44	31/19	1.72	-0.02
1, 5% Sb/Sn 280 nm	50	502	4.3	24	41/37	9/7.5	2.08	0.34
2, 9% Sb/Sn 285 nm	42	495	6.2	21	38/35	8/7	2.00	0.26
3, 13% Sb/Sn 270 nm	37	492	7.7	19	37/34	7/6	1.95	0.21
4, 12% Sb/Sn 440 nm	27	491	10	13	33/28	6/6	2.08	0.34
5, 9% Sb/Sn 445 nm	32	491	9	15.5	34/29	7/6	2.06	0.32

Table 3

Example	Green glass, 6 mm, LT/ET glass alone = 2.02							
	LTC	λ_D tr	P	ET	SF	LR	LT/ET	% difference
Comparative 1	24	561	13	13	28/33	34/14	1.85	-0.17
Comparative 2	42.6	540	6.5	20.7	35/39	31/15	2.06	0.04
1', 5% Sb/Sn 280 nm	43	504	5.8	18.4	36/32	8.5/7	2.34	0.32
2', 9% Sb/Sn 285 nm	36	498	7.4	15.7	34/31	7.7/6	2.29	0.27
3', 13% Sb/Sn 270 nm	32	495	8.8	14	33/30	7/6	2.29	0.27
4', 12% Sb/Sn 440 nm	23	463	11.5	10	31/26	6/5	2.30	0.28
5', 9% Sb/Sn 445 nm	27	493	10	12	32/27	7/6	2.25	0.23

EXAMPLES 6 to 10

In Examples 6 to 10, the process of Examples 1 to 5 is followed but with dark green glass as defined in Table 1, with a thickness of 4 mm or, as an alternative form, of 6 mm:

Table 4:

Example	Dark green glass, 4 mm, LT/ET glass alone = 1.88									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
6, 5% Sb/Sn 280 nm	35	496	9	16.5	35/31	8/6	2.12	0.24	13%	
7, 9% Sb/Sn 285 nm	30	493	11	14	33/30	7/6	2.14	0.26	14%	
8, 13% Sb/Sn 270 nm	26	491	12	13	32/30	7/5	2.00	0.12	6%	
9, 12% Sb/Sn 440 nm	19	491	15	9	30/25	6/5	2.11	0.23	12%	
10, 9% Sb/Sn 445 nm	23	491	13	10.5	30/26	7/5	2.19	0.31	17%	

Table 5:

Example	Dark green glass, 6 mm, LT/ET glass alone = 2.20									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
6', 5% Sb/Sn 280 nm	26	497	12	10.5	30/26	8/5	2.48	0.28	13%	
7', 9% Sb/Sn 285 nm	22	495	14	9	29/26	7/5	2.44	0.24	11%	
8', 13% Sb/Sn 270 nm	19	493	15	8	29/26	7/5	2.38	0.18	8%	
9', 12% Sb/Sn 440 nm	14	492	18	6	27/23	6/5	2.33	0.13	6%	
10', 9% Sb/Sn 445 nm	16	492	16	6.8	28/23	7/5	2.35	0.15	7%	

It is observed that the selectivity is markedly increased: from 6 to 17% for glass with a thickness of 4 mm, and, furthermore, the dominant transmitted wavelength is less than that of the coating-free coloured glass.

EXAMPLES 11 to 15

- 5 In Examples 11 to 15, the process of Examples 1 to 5 is followed but with very dark green glass as defined in Table 1, with a thickness of 4 mm or, as an alternative form, of 6 mm:

Table 6:

Example	Very dark green glass, 4 mm, LT/ET glass alone = 1.94									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
11, 5% Sb/Sn 280 nm	25	495	13	11.5	31/27	8/5	2.14	0.20	10%	
12, 9% Sb/Sn 285 nm	21	493	14	10	30/27	7/5	2.08	0.14	7%	
13, 13% Sb/Sn 270 nm	19	491	16	9	30/27	7/5	2.00	0.06	3%	
14, 12% Sb/Sn 440 nm	14	491	18	6.4	28/23	6/5	2.00	0.06	3%	
15, 9% Sb/Sn 445 nm	16	491	17	7.4	28/23	7/5	2.07	0.13	6%	

Table 7:

Example	Very dark green glass, 6 mm, LT/ET glass alone = 2.24									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
11', 5% Sb/Sn 280 nm	16	495	17	6.3	27/22	8/5	2.54	0.30	13%	
12', 9% Sb/Sn 285 nm	13	494	19	5.4	27/23	7/5	2.41	0.17	7%	
13', 13% Sb/Sn 270 nm	12	493	20	4.8	27/23	7/5	2.50	0.26	12%	
14', 12% Sb/Sn 440 nm	8.7	492	22	3.5	26/21	6/4	2.49	0.25	11%	
15', 9% Sb/Sn 445 nm	10	492	21	4.1	26/21	7/5	2.44	0.20	9%	

The selectivity is improved and the dominant transmitted wavelength is less than that of the uncoated coloured glass. It may be noted that the percentage increase in the selectivity is less than the percentage increase obtained in the preceding examples. However, it is necessary to take into account the starting light transmission when the selectivities are compared: the lower the starting light transmission, the more difficult it is to increase the selectivity.

EXAMPLES 16 to 20

In Examples 16 to 20, the process of Examples 1 to 5 is followed but with "blue 1" glass as defined in Table 1, with a thickness of 4 mm:

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Table 8:

Example	Blue 1 glass, 4 mm, LT/ET glass alone = 1.74									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
16, 5% Sb/Sn 280 nm	34	488	15	17	35/31	8/6	2.00	0.26	15%	
17, 9% Sb/Sn 285 nm	28	487	17	15	34/30	8/5	1.87	0.13	7%	
18, 13% Sb/Sn 270 nm	25	486	19	13	33/30	7/5	1.92	0.18	11%	
19, 12% Sb/Sn 440 nm	18	486	21	9.3	30/25	6/5	1.94	0.20	11%	
20, 9% Sb/Sn 445 nm	22	486	20	11	31/26	7/5	2.00	0.26	15%	

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The selectivity is markedly increased, whereas the dominant transmitted wavelength, situated in the blue region, is slightly decreased.

EXAMPLES 21 to 25

In Examples 21 to 25, the process of Examples 1 to 5 is followed but
5 with "blue 2" glass as defined in Table 1, with a thickness of 4 mm:

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Table 9:

Example	Blue 2 glass, 4 mm, LT/ET glass alone = 1.86									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
21, 5% Sb/Sn 280 nm	30	486	21	14	33/29	8/5	2.14	0.28	15%	
22, 9% Sb/Sn 285 nm	25	484	23	12	32/28	7.5/5	2.08	0.22	12%	
23, 13% Sb/Sn 270 nm	22	484	25	11	31/28	7/5	2.00	0.14	8%	
24, 12% Sb/Sn 440 nm	16	484	27	8	29/24	6/5	2.00	0.14	8%	
25, 9% Sb/Sn 445 nm	19	484	26	9.2	30/25	7/5	2.07	0.21	11%	

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The selectivity is markedly increased, whereas the dominant transmitted wavelength remains identical or decreases.

EXAMPLES 26 and 27

For Example 26, the process of Example 1 is followed with "grey 1" glass as defined in Table 1. For Example 27, the glass is "grey 2" glass as defined in Table 1.

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Table 10:

Example 26	Grey 1 glass, 4 mm, LT/ET glass alone = 1.39									
Example 27	Grey 2 glass, 4 mm, LT/ET glass alone = 1.43									
	LTC	λ_p tr	P	ET	SF	LR	LT/ET	difference	% difference	
26, 5% Sb/Sn 280 nm	28	495	6	15.9	30.3	5/7.1	1.76	0.37	27%	
27, 5% Sb/Sn 280 nm	37.9	496	5.2	21.3	34.6	5.7/4.4	1.78	0.35	24%	

The selectivity is very markedly increased with respect to the selectivity of the uncoated coloured glass.

EXAMPLES 28 to 43

These examples are presented in Tables 11 and 12. The coloured glasses used are mentioned in the second column of the table. The coloured glasses are those defined in Table 1. Furthermore, the blue glass "Azurlite" is used in Examples 42 and 43. This glass has the properties mentioned in Table 12. Its content of colouring agents is as follows:

0.41% Fe_2O_3 with 0.255% FeO (Fe^{2+} /total Fe greater than 60%),
0.35-0.56% CeO_2
0.010% SO_3 .

The stackings of deposited layers are as follows:

- an underlayer of tin oxide with a thickness of 29 nm, then a layer, deposited by pyrolysis, based on tungsten oxide comprising 9.4% of Na with a thickness of 34 nm, covered with an SnO_2 layer with a thickness of 25 nm,
- an underlayer of tin oxide with a thickness of 16 nm, then a layer, deposited by pyrolysis, based on tungsten oxide comprising 9.4% of Na with a thickness of 78 nm, covered with an SnO_2 layer with a thickness of 40 nm,
- a "low emissivity" stacking comprising an SiO_x layer with a refractive index of 1.68 and a thickness of 70 nm coated with a low emissivity layer ($\epsilon = 0.15$) of tin oxide SnO_2 doped with fluorine (1 to 2% of fluorine) with a thickness of 320 nm. For the latter example, the values are measured with the layer in the 2 position, i.e. glass side, in order to benefit from the favourable effect of the low emissivity layer on the solar factor. In contrast, for all the other types of stackings, the values are measured with the layer in position 1 (coating side).

EXAMPLES 44 and 45

These examples are presented in Table 12. The coloured glasses used are the very dark green and dark green glasses defined in Table 1. The coating is formed of an absorbent stacking, with a thickness of the order of 75 nm, composed of a layer comprising essentially TiN and of a layer of SiC. The properties are measured with the layer in position 1 (coating side).

Table 11

Exam- ple		LTC	ET	SF	LT/ET	Diff.	% diff.	LT/SF	Diff.	% diff.	λ_D tr	P
	Support: blue 2 glass, 4 mm	39.9	21.4	40.1	1.86			0.99			486	24
28	GL/SnO ₂ (29)/WO ₃ Na9.4(34)/SnO ₂ (25)	37.4	18.7	29.7	2.00	0.14	8	1.26	0.27	28	485	21
29	GL/SnO ₂ (16)/WO ₃ Na9.4(78)/SnO ₂ (40)	21.1	10.5	18	2.0	0.15	8	1.17	0.19	19	484	24.7
30	GL/SiO _x 1.68(70)/SnO ₂ .F(320) #2	37.2	19.7	31.9	1.89	0.03	2	1.17	0.18	18	485	19.6
	Support: green glass, 4 mm	67	38.6	53	1.74			1.27			504	3.5
31	GL/SnO ₂ (29)/WO ₃ /Na9.4(34)/ SnO ₂ (25)	62.8	33.1	41.5	1.90	0.16	9	1.51	0.25	20	497	5.2
32	GL/SnO ₂ (16)/WO ₃ Na 9.4(78)/SnO ₂ (40)	35.4	17.6	23.9	2.01	0.27	16	1.48	0.22	17	492	8.5

Table 11 cont.

Exam- ple		LTC	ET	SF	LT/ET	Diff.	% diff.	LT/SF	Diff.	% diff.	λ_p tr	P
	Support: very dark green glass, 4 mm	34.3	17.7	37.3	1.94			0.92			496	11.2
33	GL/SnO ₂ (29)/WO ₃ /Na9.4 (34)/SnO ₂ (25)	32.2	15.2	26.8	2.12	0.18	9	1.20	0.29	32	494	12.8
34	GL/SnO ₂ (16)/WO ₃ Na 9.4(78)/SnO ₂ (40)	18.1	8.1	16	2.23	0.29	15	1.13	0.22	25	492	15.8
	Support: dark green glass, 4 mm	47.5	25.2	42.9	1.88			1.11			498	7.7
35	GL/SnO ₂ (29)/WO ₃ /Na9.4 (34)/SnO ₂ (25)	44.5	21.4	31.9	2.08	0.20	11	1.30	0.30	27	496	9.4
36	GL/SnO ₂ (16)/WO ₃ Na 9.4(78)/SnO ₂ (40)	25.1	11.6	18.9	2.16	0.28	15	1.33	0.23	21	493	12.4
	Support: grey 2 glass, 4 mm	49.4	34.6	49.9	1.39			0.84			495	5
37	GL/SnO ₂ (29)/WO ₃ /Na9.4 (34)/SnO ₂ (25)	46.3	26.7	36.3	1.73	0.30	21	1.28	0.29	29	492	6.9
38	GL/SnO ₂ (16)/WO ₃ Na9.4 (78)/SnO ₂ (40)	26	13.8	20.8	1.88	0.45	32	1.25	0.26	27	489	10.3

Table 12

Exam ple		LTC	ET	SF	LT/ET	Diff.	% diff.	LT/SF	Diff.	% diff.	λ_0 tr	P
	Support: grey 1 glass, 4 mm	36.5	26.3	43.7	1.39			0.84			494	5.8
39	GL/SnO ₂ (29)/WO ₃ Na9.4(34)/SnO ₂ (25)	34.2	20.4	31.1	1.68	0.29	21	1.10	0.27	33	492	7.7
40	GL/SnO ₂ (16)/WO ₃ Na9.4(78)/SnO ₂ (40)	19.2	10.6	18.1	1.81	0.42	30	1.06	0.23	28	489	11.1
41	GL/SiO _x 1.68(70)/SnO ₂ .F(320) #2	34.1	24.1	35.6	1.41	0.03	2	0.96	0.13	16	493	5.3
	Support: blue glass, Azurite (4 mm)	76.5	44	56.9	1.74			1.34			488	8.6
42	GL/SnO ₂ (29)/WO ₃ / Na9.4(34)/SnO ₂ (25)	71.8	39	46.4	1.84	0.10	6	1.55	0.20	15	487	10.4
43	GL/SnO ₂ (16)/WO ₃ Na 9.4(78)/SnO ₂ (40)	40.6	20.8	26.5	1.95	0.21	12	1.53	0.19	14	486	14
	Support: very dark green glass, 4 mm	34.3	17.7		1.94						496	11.2
44	GL/TiN/SiC	20.4	9.4		2.17	0.23	12				493	16.2
	Support: dark green glass, 4 mm	47.5	25.2		1.88						498	7.7
45	GL/TiN/SiC	28.2	13.2		2.14	0.26	14				494	12.9